



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 6 :</b> <b>C07C 69/653, C08F 20/22, G02B 1/04, 6/16</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/18785</b> <b>(43) International Publication Date:</b> 13 July 1995 (13.07.95)
<b>(21) International Application Number:</b> PCT/GB94/02773 <b>(22) International Filing Date:</b> 3 January 1995 (03.01.95)  <b>(30) Priority Data:</b> 9400016.3 4 January 1994 (04.01.94) GB  <b>(71) Applicant:</b> MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55144 (US).  <b>(71)(72) Applicant and Inventor:</b> DODDS, Alastair [GB/GB]; Minnesota 3M Research Limited, Pinnacles, Harlow, Essex CM18 6EE (GB).  <b>(72) Inventors:</b> STACEY, Nicholas; 2 Elm Cottages, High Easter, Essex CM1 4QL (GB). WILLIAMS, Luke; Minnesota 3M Research Limited, Pinnacles, Harlow, Essex CM18 6EE (GB).  <b>(74) Agent:</b> BOWMAN, Paul, Alan; Lloyd Wise, Tregear & Co., Norman House, 105-109 Strand, London WC2R 0AE (GB).		<b>(81) Designated States:</b> CA, CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> 2-FLUOROACRYLATE ESTER POLYMERS AND USE THEREOF AS OPTICAL MATERIALS		
<b>(57) Abstract</b>  1H, 1H-perfluorocyclohexylmethyl 2-fluoroacrylate, homopolymers and copolymers thereof. The copolymers may comprise monomers selected from: a) at least 40 % by weight of 1H, 1H-perfluorocyclohexylmethyl 2-fluoroacrylate, and b) up to 60 % by weight of monomer selected from methyl 2-fluoroacrylate, 1H, 1H-perfluoroacetyl 2-fluoroacrylate, 1H, 1H-perfluoro(2-(butoxy)propyl) 2-fluoroacrylate and any combination thereof.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

2-Fluoroacrylate Ester Polymers and Use  
Thereof As Optical Materials

This invention relates to the ester of  
2-fluoroacrylic acid with 1H,1H,-perfluorocyclohexyl-  
5 methanol and to homopolymers and copolymers thereof and  
to the use of such polymers in optical materials,  
particularly optical fibres.

Plastic optical fibres have attracted much interest  
and been an area of active commercial research for many  
10 years since they offer the potential of combining the  
rapid data transmission advantages afforded by glass  
optical fibres with the ruggedness and low costs  
associated with copper cabling products.

Despite this activity and interest, plastic optical  
15 fibres (POFs) have not, to date, been widely accepted as  
a data communications medium. One of the key  
contributing factors in delaying this acceptance has been  
the poor thermal stability of available fibres. Data  
transmission systems in both automotive and aerospace  
20 applications provide large markets for POFs. However,  
underbonnet applications in automobiles require extended  
performance above 100°C, with many aerospace environments  
even more severe and demanding performance at  
temperatures in excess of 140°C. The upper use  
25 temperature for current commercial POFs, which are  
predominantly based on polymethyl methacrylate (PMMA) and  
polystyrene [PS], is about 80°C, which is too low for  
these applications. The high temperature performance of  
a polymer for these applications is limited by its glass  
30 transition temperature (Tg), since at temperatures around  
and above Tg its mechanical and optical properties  
decline. For both PMMA and PS, Tg is in the range of  
100°C to 105°C. Thus, materials with Tgs above those of  
PMMA and PS are desirable to increase the maximum use  
35 temperature of the resulting POFs.

A further factor delaying the acceptance of POFs has been the high optical attenuations of currently available commercial fibres to transmission in the red and near infrared (NIR) region, where preferred solid state light sources operate. The fabrication of plastic optical fibres with lower attenuations in these regions is an area of current polymer fibre research.

The predominant contributor to the red and NIR optical attenuation of most amorphous polymeric materials suitable for optical fibres is absorption caused by overtone and combination bands of the C-H bond's fundamental vibration. The academic and patent art has therefore concentrated on reducing these attenuations and this has been achieved by partial or complete replacement of H atoms by the heavier deuterium or halogen atoms. This reduces NIR attenuations due to the higher reduced mass of the C-X bond (X=D,F,Cl) compared to the C-H bond, so shifting the fundamental and overtone frequencies out of the range of interest.

The replacement of H with D has received much attention and has produced very good results (Appl.Phys.Let. 1983, 42, 567). Attenuations as low as 20 dB/Km (650nm) have been obtained from fully deuterated PMMA fibres. Unfortunately, cost considerations of deuteration make this approach essentially of academic interest only, and there has been no attempt to commercialise a fibre containing deuterium.

Halogenation represents a much more commercially attractive option to reducing attenuations. By introduction of these heavier atoms, the effect of hydrogen overtones can be reduced and/or diluted and so attenuations may be reduced in a similar manner to deuteration. Whilst both chlorine and bromine substituted polymers have been considered, the advantages associated with fluorination, namely, C-F bond stability, low atomic bulk etc., have made this approach the most attractive.

For a number of reasons, mainly related to fabrication and processing, optical polymers are predominantly acrylic ester based materials. Fluorination in such systems has been largely achieved by the use of short-chain perfluorinated ester methacrylates, taking advantage of the readily available short chain perfluoroalcohols. A review of this art is disclosed in WO 93/03074. The attenuation improvements available from such materials, particularly in the NIR can be significant. The above document discloses materials with NIR attenuations approximately 25% of those of conventional PMMA fibres. However, in order to reduce attenuations substantially further, not only must the side chain ester functionality of the polymer be fluorinated, but it is also necessary to replace the hydrogen atoms of the polymer backbone. One of the most effective methods of achieving this is to replace the methyl function of the methacrylate backbone with a fluorine atom, producing 2-fluoroacrylate polymers. As well as reducing the polymer H-atom content, this approach also has the advantage that, by careful choice of the side-chain group, the Tg of the polymer may be increased to a level where it may be suitable for high temperature usage. The combination of high Tg, leading to a high upper use temperature, and a high degree of fluorination, giving the potential for very low optical losses, yields materials which show much promise as optical fibre core materials for local area networks where the use conditions are severe, for example in automobile and aerospace applications.

Esters of 2-fluoroacrylic acid are well known. The methyl ester of 2-fluoroacrylic acid can be prepared by the reaction of methyl 2-fluoroacetate with formaldehyde in the presence of calcium hydride and dimethyl oxalate, as disclosed in Macromolecules 1980, 13, 1031-1036. The polymerisation of this monomer, methyl 2-fluoroacrylate (MFA), is reported to give a high Tg (128°C) polymer.

Several methods are known for the preparation of other derivatives of 2-fluoroacrylic acid e.g.

J. Fluorine Chem. 1991, 55, 149-162. For example, 2H-octafluorocyclopentyl methyl 2-fluoroacrylate may be prepared from 2,3-difluoropropionyl chloride by a two-step reaction in which the acid chloride is dehydrofluorinated to give the 2-fluoroacryloyl chloride, then treated with 1H,1H,2H-octafluoropentyl methanol in the presence of base. There is no disclosure of polymerisation of this or other monomers although reference is made to the good general optical and physical properties of 2-fluoroacrylic ester polymers.

It is known that polymers containing 2-fluoroacrylate esters may be used for the preparation of optical fibre cores. EP-0128516 discloses monomers of the formula  $H_2C=CF-COOR_f$ , in which  $R_f$  is a fluorine-containing aliphatic group, preferably a fluorine-containing lower alkyl group. Examples are given of 2-fluoroacrylate homopolymers with glass transition temperatures up to 125°C [poly (3H-1,1-dimethyl-tetrafluoropropyl 2-fluoroacrylate)]. JP 02092908 discloses 2-fluoroacrylates in which the backbone C-H bonds are replaced by C-D bonds to reduce the NIR bond absorptions. The monomers have the formula  $D_2C=CR^1-COOR^2$ , in which  $R^1$  is F, D, or  $CD_3$ , and  $R^2$  is  $C_nY_{2n+1}$  ( $Y=F, Cl$ ). Lower alkyl chains only are exemplified.

Monomers and polymers of 2-fluoroacrylates with fluorinated rings are disclosed in FR 2623510. However, the examples and claims relate only to fluorinated aromatic materials.

AU-A-13035/88 discloses 2-fluoroacrylate materials in which a substituted bicyclic ring is present. The monomer structure allows the possibility of bicyclic perfluorinated 2-fluoroacrylate esters, however, all examples relate to chlorinated monomers. The patent recommends specifically chlorine, bromine or trifluoromethyl substitution, but discloses no

perfluorinated rings.

Other examples of polymers of alicyclic highly fluorinated (meth)acrylic monomers are known as optical materials. WO93/03074 discloses a specific monomer, 1H, 1H-perfluorocyclohexylmethyl methacrylate, and homopolymers and copolymers thereof with other fluorinated and non-fluorinated monomers, as an optical fibre core with low optical loss. However, high temperature usage is not disclosed.

US-5148511 discloses cladding compositions comprising copolymers of fluorine containing methacrylate monomers with methyl methacrylate. Glass transition temperatures of up to 108°C are indicated for solution copolymers of 1H,1H-perfluorocyclohexylmethyl methacrylate with methyl methacrylate in 50:50 weight ratio.

The present invention provides alternative fluorine-containing materials suitable for the preparation of optical elements.

According to one aspect of the invention there is provided 1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate.

According to a further aspect of the invention there is provided a homopolymer or copolymer of 1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate.

Depending on the intended use and desired physical properties, the copolymer may comprise, in addition to 1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate, any addition-polymerisable monomer, such as acrylic acid, methacrylic acid, 2-fluoroacrylic acid and esters, amides and nitriles derived therefrom, including mixtures of these monomers. For optical fibre applications, the copolymer is preferably formed from:

a) at least 40%, preferably at least 60% by weight of 1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate and

- b) up to 60% by weight, preferably 0 to 40% by weight of a copolymerisable monomer selected from the group consisting of methyl 2-fluoroacrylate, 1H,1H-perfluorooctyl 2-fluoroacrylate, 1H,1H-perfluoro(2-  
5 (butoxy)propyl) 2-fluoroacrylate, or other similar monomers, or a mixture of such monomers.

The polymers of this invention may be used to form the core of plastic optical fibres e.g. by the techniques disclosed in WO93/03074. Generally the process for the  
10 preparation of POFs comprises the following steps:

- a) the monomer mixture, together with a free radical initiator and chain transfer agent, is placed in a closed reaction vessel;
- b) the polymerisable mixture is degassed;
- 15 c) the temperature of the vessel is raised, resulting in polymerisation of the monomer mixture;
- d) the polymer is extruded into a fibre core generally having a diameter in the range of 0.1 to 2.0 mm.

20 The plastic fibres of the invention exhibit NIR attenuations which are significantly lower than the best commercially available materials based on PMMA (typical losses about 3000 dB/km at 840 nm). To a first order of approximation, attenuations in such fibres can be related  
25 to the H atom concentration in relation to PMMA. By carrying out such a calculation, it is estimated that the attenuation of fibres of this invention should be approximately 150 dB/km at 840 nm. Further, whilst PMMA attenuations are highly sensitive to small wavelength  
30 drifts of the light source in this region, the fluorinated fibre of this invention is comparatively insensitive to these effects.

However the key advantage of using the perfluoro-cyclohexyl functionality stems from the observation that  
35 this grouping can also impart high glass transitions (about 140°C) to the resulting polymers and fibres. This is an important feature; straight or branched

perfluoroalkyl side chains are not able to achieve the high glass transitions afforded by this polymer. These Tgs are comparable to many fibres claimed for use in high temperature applications. Polycarbonates (Tg 130 to 160°C), for example, have been used as high temperature POFs, but these materials can not be bulk polymerised from a pure monomer mixture and contain contaminants which are difficult to eliminate from the polymer, resulting in high optical attenuations in the fibres produced. Alkyl methacrylates with alicyclic substituents (e.g. bornyl, fenchyl, menthyl) have also been used for high temperature fibres; again their properties are not acceptable for low attenuation applications due to their high C-H bond content and resulting high optical losses.

In comparison with these other polymers which have been used as high temperature POFs, the materials of this invention show a very desirable combination of properties. Additionally, high degradation temperatures (about 350°C) are generally observed in 2-fluoroacrylate polymers, which aids their processing and increases thermal stability above that observed for their methacrylate analogues.

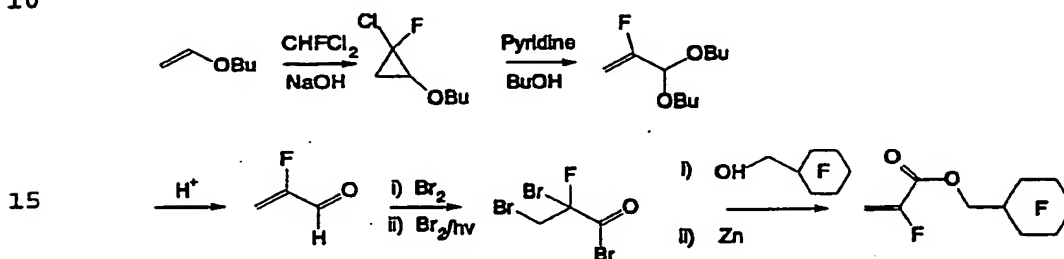
In addition, the fibres of the invention have excellent physical properties when compared to other highly fluorinated polymer materials which have been reported as low attenuation materials. Those described in WO93/03074, for example, where the perfluorocyclohexyl functionality is substituted onto a methacrylate backbone, are lower in modulus and more brittle than those of this invention.

The physical properties, together with a high degree of thermal stability (both in terms of upper use temperature and decomposition temperature), and potential for low attenuation, give a combination of properties which have not been reported previously for any comparable material.

The polymers of the invention could also find utility in the preparation of other high performance optical components e.g. optical fibre claddings, lenses and other forms of waveguides, where similar properties are desirable.

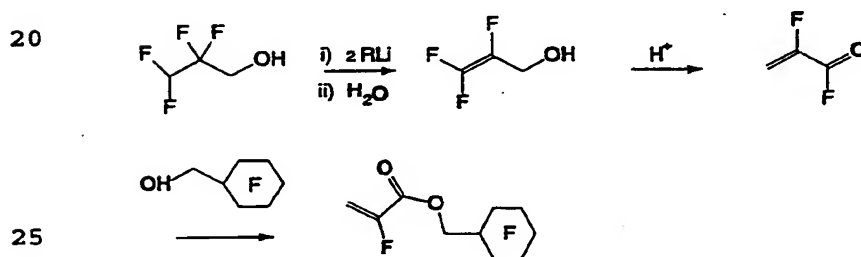
1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate may be prepared according to modifications of standard literature procedures (Synthesis, 1985, 754; J.Org.Chem. 1989, 54, 5640), as outlined in either Scheme 1 or Scheme 2.

10



Scheme 1

20



25

Scheme 2

In which  represents perfluorocyclohexyl

30

The invention will now be illustrated by the following Examples:-

#### Example 1

a) Preparation of [1H,1H-perfluorocyclohexylmethyl 2,3-dibromo-2-fluoropropanoate]

35

2,3-dibromo-2-fluoropropanoyl bromide (158g, 0.5mol) was added dropwise to a stirred solution of 1H,1H-

perfluorocyclohexylmethanol (150g, 0.48mol) and triethylamine (53.3g, 0.52mol) in dichloromethane (250ml) at 0°C. The mixture was allowed to attain room temperature and was then stirred overnight. Work-up was achieved by washing with water (3 x 250ml) and brine (250ml). After drying (MgSO<sub>4</sub>) and removing solvents under a vacuum, the organic residue was chromatographed through basic alumina using a 40-60°C petroleum spirit fraction as the eluent. Removal of solvents left the title compound as a crude oil (yield = 233g).

b) Preparation of 1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate by Scheme 1.

Zinc powder (36g, 0.5mol) was added to diisopropyl ether (175ml) and the mixture was purged with argon. The reaction mixture was brought to reflux and 1H,1H-perfluorocyclohexylmethyl 2,3-dibromo-2-fluoropropanoate (100g, 0.18mol) was added dropwise. Reflux was continued for six hours before the reaction mixture was allowed to cool. Zinc was removed by filtration and solvents were removed under vacuum. The residue was redissolved in ether (250ml) and washed with water (2x100ml), brine (100ml) and then dried (MgSO<sub>4</sub>). After removal of solvents, a small quantity of phenothiazine inhibitor (10mg) was added and the crude mixture was distilled, to give the title compound (yield - 72g, Bpt. 45-65°C/0.5mmHg) as a clear oil. Further purification of the material for use in optical fibre applications was carried out by fractional distillation, giving a pure sample of the desired monomer (Bpt. 70-73°C/12mBar).

c) Preparation of 1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate by Scheme 2.

10

2-Fluoroprop-2-enoyl fluoride (16.2g, 1.1 eq) was dissolved in dichloromethane (100ml) and the solution was cooled to -50°C, with stirring. To this was added, dropwise, a solution of 1H,1H-perfluorocyclohexylmethanol (50g, 1 eq), triethylamine (17.45g, 1.1 eq) and N,N-dimethylaminopyridine (10mol%) in dichloromethane (100ml). On complete addition (20 minutes approximately), the yellow reaction mixture was allowed to attain room temperature over 2 hours, before stirring overnight. Work-up of the reaction mixture at this stage was carried out by dilution of the mixture (200ml dichloromethane) and washing of the organic phase with water (2x100ml), dilute hydrochloric acid (2x50ml, 1M), water (2x100ml) and brine (100ml). The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated under vacuum to give a crude oil, purified by distillation to give the title compound (yield 55g, Bpt. 62-74°C/12mBar). Again, further purification in a similar manner to that described above, was used to purify the monomer to the level required for optical fibre preparation.

#### Example 2

25 Preparation of Poly (1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate) and processing to optical fibre.

The monomer was bulk polymerized in glass preform tubes as described in WO93/03074, using t-butylhydroperoxide as initiator (0.1 mol %) and butanethiol as chain transfer agent (0.2 mol %). The monomer was degassed in the preform tube using the method of freeze/thawing until a minimum of bubbles were generated in the monomer on thawing. The polymerisation was carried out in a fluidised sand bath under the following conditions: Initial temperature 138°C, 16 hours; ramp to 160°C at 10°C/minutes and hold for 24 hours. On completion of the

polymerisation, the preform was transferred to a fibre drawing tower such that minimum cooling occurred. The initial temperature of the drawing furnace was 180°C and an overpressure of 0.16 atmosphere of nitrogen was applied to the top of the preform. The furnace temperature was increased in 2-3°C increments until the polymer showed onset of flow (207°C). Fibre was drawn at a haul-off rate of 1.0 m/min. Attenuation measurements were made on the fibre by the method of cut backs (similar to that of BS6558 Part 1 - Optical Fibres and Cables); laser light was injected into the end of the fibre and several cutbacks were made.

The optical attenuation, measured using a Bentham Spectrophotometer and corrected to the laser measured attenuation recorded at 633 nm, showed a typical value of approximately 1400 dB/Km in the important 840 nm window.

The accompanying Figure 1 indicates the attenuation spectrum for poly (1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate), compared with that for PMMA. This shows that a large scatter wedge is present for the former material compared to the optimised PMMA fibre. Even so, the optical losses for the material of this invention are significantly lower than those of PMMA at wavelengths above 800nm.

The fibre was analysed for physical properties such as tensile strength, elongation etc; these details are given below:

Modulus	Tensile Strength (at yield)	Elongation (at yield)
1500 MPa	44.0 MPa	4.7%

Thermal analysis was also carried out on samples of the material produced above. The glass transition temperature, measured by differential scanning calorimetry at a ramp rate of 10°C/min, was 138° (midpoint); the decomposition onset was measured as

360°C by thermogravimetry, using a ramp rate of 30°C/min in a N<sub>2</sub> atmosphere.

Example 3 (comparative)

Poly(methyl methacrylate)

5       The monomer was bulk polymerised in a similar manner to that used in Example 2, using 2,2'-azobis(t-butane) as initiator (0.1 mol%) and butanethiol as chain transfer agent (0.25 mol%). After degassing the mixture, polymerisation was carried out in a silicone oil bath  
10       under the following conditions: initial temperature 130°C, 16 hours; ramp to 160°C at 10°C/hour, hold for 4 hours; ramp to 180°C at 10°C/hour, hold for 4 hours. The preform was transferred to a drawing furnace at 180°C, and an overpressure of N<sub>2</sub> was applied (0.3 atm). The  
15       temperature was increased to 202°C, and fibre was drawn from the tip of the vessel at 3 m/min.

The optical attenuation was measured by similar techniques to those used in Example 2 giving an attenuation of about 2500 db/km at 840 nm.

20       Analysis of the physical properties of the polymer fibres was also carried out by similar methods to those used in Example 2. The results are given below:

	Modulus	Tensile Strength (at yield)	Elongation (at yield)
25	3070 MPa	112 MPa	3.6%

30       Thermal analysis was also carried out, giving a glass transition temperature of 105°C and a decomposition onset of 290°C.

Example 4 (comparative)

Poly (1H,1H-perfluorocyclohexylmethyl methacrylate)

35       The monomer was bulk polymerised, and then processed to an optical fibre in a similar manner to that used in WO93/03074, Example 5.

Attenuation measurements made on the fibre indicated that the optical attenuation at 840 nm was approximately 850 db/km.

Analysis of the physical properties of the polymer fibre was not attempted due to the extreme brittleness of the fibre produced. However, thermal analysis was  
5 carried out, giving a glass transition temperature of 80°C and a decomposition onset of 200°C.

Example 5 (comparative)

Poly (1H,1H-perfluorocyclohexylmethyl methacrylate-  
10 co-methyl methacrylate).

The monomers (ratio by weight 70:30, 1H,1H-perfluorocyclohexylmethyl methacrylate:methyl-methacrylate) were bulk polymerised, and then processed to an optical fibre in a similar manner to that used in  
15 WO93/03073, Example 1.

Attenuation measurements made on the fibre indicated that the optical attenuation at 840 nm was approximately 1000 db/km.

Analysis of the physical properties of the polymer fibre attempted by similar methods to those used in  
20 Example 1. The results are given below:

	Modulus	Tensile Strength (at yield)	Elongation (at yield)
25	680 MPa	17.2 MPa	4.5%

Thermal analysis was carried out, giving a glass transition temperature of 93°C and a decomposition onset of 250°C.

30 The data given in the Examples illustrates the advantages of POFs made from poly (1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate) in accordance with the invention.

Compared to PMMA, the fibres of the invention show a  
35 higher Tg and decomposition onset, with reduced attenuation in the NIR region, and the potential for far lower attenuations with optimisation of the polymerisation and process conditions.

It can be seen that fibres of the present invention display improved thermal and physical properties in comparison with fibres described in Examples 4 and 5, which are based on methacrylate functionalised polymers.

CLAIMS

1. 1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate.
2. A homopolymer of 1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate.
- 5 3. A copolymer of 1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate.
4. A copolymer as claimed in Claim 3 formed from:
  - a) at least 40% by weight of 1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate, and
  - 10 b) up to 60% by weight of monomer selected from methyl 2-fluoroacrylate, 1H,1H-perfluorooctyl 2-fluoroacrylate, 1H,1H-perfluoro(2-(butoxy)propyl) 2-fluoroacrylate and any combination thereof.
5. A copolymer as claimed in Claim 4 comprising of at  
15 least 60% of 1H,1H-perfluorocyclohexylmethyl 2-fluoroacrylate.
6. A plastic optical fibre having a core formed of a polymer as claimed in any one of Claims 2 to 5.
7. A plastic optical fibre as claimed in Claim 6 having  
20 a diameter in the range 0.1 to 2.0mm.
8. An optical component comprising a polymer as claimed in any of Claims 2 to 5.

1/1

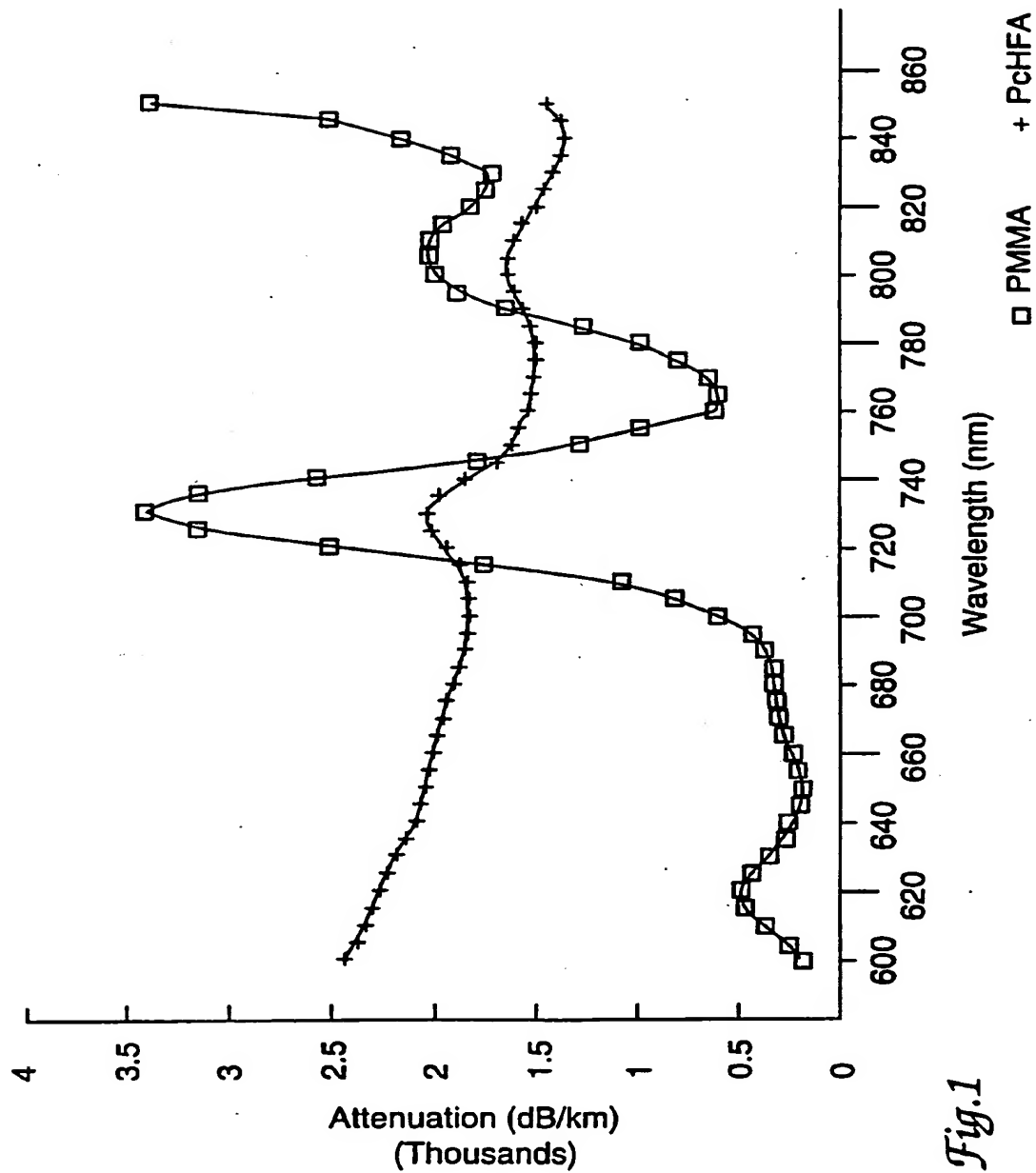


Fig.1

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 94/02773

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C07C69/653 C08F20/22 G02B1/04 G02B6/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,93 03074 (MINNESOTA MINING AND MANUF. CO.) 18 February 1993 cited in the application	1
A	US,A,5 148 511 (P. SAVU ET AL.) 15 September 1992 cited in the application	1
A	EP,A,0 128 516 (DAIKIN KOGYO CO., LTD) 19 December 1984 cited in the application	1
A	AU,B,13 035 (HOECHST AG) 15 September 1988 cited in the application	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*A\* document member of the same patent family

Date of the actual completion of the international search

31 March 1995

Date of mailing of the international search report

26.04.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Glikman, J-F

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/GB 94/02773

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9303074	18-02-93	US-A- 5223593 EP-A- 0597887 JP-T- 7502127	29-06-93 25-05-94 02-03-95
US-A-5148511	15-09-92	AU-A- 2790492 CA-A- 2120334 EP-A- 0611365 JP-T- 7500856 WO-A- 9309065	07-06-93 13-05-93 24-08-94 26-01-95 13-05-93
EP-A-0128516	19-12-84	JP-C- 1626250 JP-B- 2050442 JP-A- 59227908 DE-A- 3484883	28-11-91 02-11-90 21-12-84 12-09-91
AU-B-13035		NONE	